Site Need Statement

| General Reference Information | | |
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| 1 * | Need Title: Technetium-99 Analysis In Hanford Tank Waste | |
| 2 * | Need Code: RL-WT001 | |
| 3 * | <i>Need Summary:</i> An accurate, robust production laboratory method for the measurement of technetium-99 (⁹⁹ Tc) concentration in Hanford Site waste tank matrices is needed. New TPA (Tri-Party Agreement) strategy has Hanford tanks being sequenced for retrieval based on environmental risk. For tank S-112, ⁹⁹ Tc is the main driver for risk. Assumptions for Tc ⁹⁹ solubility significantly impact the risk results for allowable leak loss during retrieval, as well as allowable residuals after retrieval. Methods for evaluating and verifying the solubility and mobility of contaminates of concern, such as Tc ⁹⁹ , during retrieval and post retrieval operations is critical for developing risk based Leak detection, monitoring and mitigation strategies for SST retrieval. Methods must provide a high level of confidence to resolve risk uncertainties associated with tank farm retrieval performance evaluations | |
| 4 * | Origination Date: FY 2000 | |
| 5 * | <i>Need Type:</i> Technology Opportunity The site desires an alternative to the current or planned baseline technology/process (e.g., a baseline exists but can be improved). | |
| 6 | Operation Office: Office of River Protection (ORP) | |
| 7 | Geographic Site Name: Hanford Site | |
| 8 * | Project: Retrieval and Closure PBS No: RL-TW04 and RL-TW11 | |
| 9 * | National Priority: 1. High - Critical to the success of the EM program, and a solution is required to achieve the current planned cost and schedule. X 2. Medium - Provides substantial benefit to EM program projects (e.g., moderate to high life-cycle cost savings or risk reduction, increased likelihood of compliance, increased assurance to avoid schedule delays). 3. Low - Provides opportunities for significant, but lower cost savings or risk reduction, may reduce the uncertainty in EM program project success. | |
| 10 | Operations Office Priority: Medium | |
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Problem Description Information

- Operations Office Program Description: The overall purpose of the Retrieve and Transfer SST Waste function is to move the waste from the SSTs into preferred storage in the DST system. A primary objective of this function is to develop and test alternative and improved retrieval technologies to past-practice sluicing. As part of this effort Leak Detection Monitoring and Mitigation (LDMM) approaches are being developed for concurrent deployment. To support this effort Cold Test Training & Mock-up Facilities are being established. The baseline end state of the Retrieve and Transfer SST Waste function is:
 - Retrieval of all wastes from the SSTs
 - The safe, environmentally compliant transfer of this waste to the DSTs
 - SSTs in a ready state for implementing closure and final disposal of the SST farms.

The overall purpose of the Closure function is to close SST and DST tank farms and RPP facilities. Closure of tanks and tank farms assumes that waste retrieval will remove sufficient waste from the tanks that the residual wastes following retrieval, the tanks themselves, the tank farm ancillary equipment, and the contaminated soil will be disposed in place in accordance with applicable regulations and agreements. This strategy also assumes that the residual waste and other tank farm source terms will be considered by the U. S. Nuclear Regulatory Commission to be incidental waste, i.e., non-high-level waste. This function has substantial involvement with studies directed at understanding contaminant migration in the vadose zone and groundwater that are part of the Hanford Groundwater/Vadose Zone (GW/VZ) Integration Project.

Need/Problem Description: An accurate production laboratory and/or field methods for establishing the 99Tc concentration in LLW is needed. 99Tc concentration is a critical component of feed to the waste vitrification vendors as well as a key risk driver that establishes values for allowable leak thresholds and residual waste limits for SST retrieval projects. The absolute accuracy of these analytical results produced at the Hanford Site has been questioned and found to be in disagreement with results produced at another U.S. Department of Energy (DOE) site. This original issue appears to be resolved based on work in FY 1998 for the high-organic-containing waste in which these differences were observed. Variability of REDOX potential and interferences present in Hanford Site tank waste can produce inconsistent performance of radiochemical sample preparation methods in use. Technetium in the +7 oxidation state is known to be mobile in the soil column and therefore, the concentration in tank waste must be known well to estimate long-term effects of waste tank leakage during storage or retrieval operations. The use of ICP/MS in place of radiochemical methods may also help resolve some of these chemical issues; however, insufficient comparison data are available to fully support the ICP/MS results. Because the ICP/MS does not require chemical separations before analysis, it is less subject to the interferences described above. However, there may be other errors associated with sample dissolution or polyatomic interferences that have not been clearly defined for this relatively new technology. Finally, when the technology is generating data that is being used to determine an impact on public/worker safety and health and is being critically reviewed by stakeholders, inter-laboratory comparisons of the measurement system are needed to raise the level of confidence in the data and credibility of the technology independent of the site at which it being used.

Failure to develop accurate and reliable measurement methods that are recognized by the regulators, stakeholders, and process operations as confident measurement systems will affect final waste processing requirements and site clean-up criteria. Needs associated to these requirements and criteria are addressed under RL-WT069, *Value of Information Decision Analysis for Tank Farm Closure*. Accurate 99Tc measurements are needed to produce effective risk assessments and ensure that vitrification processes and products will meet acceptance criteria. Failure to meet those criteria could result in additional program costs or regulatory requirements.

- ** | Program Baseline Summary (PBS) No.: TW04, TW11
 - Work Breakdown Structure (WBS) No.: 5.02.01.02.07.12 and 5.05.01.01
- TIP No.: M-45 Series Milestones for Tank Waste Closure Plans

Functional Performance Requirements: Because the method will be frequently requested in the waste disposal program, it must be appropriate for production laboratory use to routinely measure ⁹⁹Tc not only in tank waste matrices, but also in processed or treated waste. Performance requirements will vary for the different applications of the data and matrices.

For example, the estimated quantitation limit (EQL) for ⁹⁹Tc in the low-level waste (LLW) as stated in the Interface Control Document (ICD-19) is 5xE-04 \(\extbf{ZCi/mL} \). The LLW data quality objective (DQO), WIT-98-010, Table 7-2, provides a basis of the accuracy requirements which range from 10% to no accuracy requirement depending on how close it is to the average tank concentration. The minimum reportable quantity for this DQO for performance assessment is 2.0xE-2 \(\extbf{ZCi/mL} \). The relative percent difference between duplicates to support this DQO is less than 20%. Many of these DQOs are still in the draft stages and can be expected to change, but these criteria are not expected to be lessened. The method should be rapid (preferably less than 4 hours per batch for preparation and 1 hour per batch for analysis) and permit reasonably large batch sizes (4 to 10 samples + quality control samples). The use of hazardous chemicals and generation of waste should be minimized.

A validated and acceptable method will be needed to support LLW and high-level waste (HLW) feed characterization and acceptance by the Privatization vendor. The schedule for this activity is changing with the awarding of the contract to the Bechtel Northwest Group. However, if data from present characterization are to be utilized to support the certification of the waste transferred, the need is immediate. Work was completed in fiscal year (FY) 1998 that resolved the problems associated with analyzing ⁹⁹Tc in waste with high organic complexant content in which ⁹⁹Tc data were bias low because of incomplete oxidation of ⁹⁹Tc. However, there have been instances in FY 1998 where the radiochemical results are higher than the inductively coupled plasma/mass spectrometer (ICP/MS). This indicates the existing method may not be reliable in all matrices and the limits of reliability are not established. During FY 1999, investigation showed carry through of beta emitting ²⁴¹Pu, originating from chemical enhancement of plutonium in tank sludges through precipitation. While corrections were made in liquid scintillation counting. carry

through of plutonium in the chemical separation is not resolved. There are also indications in the analysis of waste from AX-104 that the regulatory acid digestion methods may not be quantitative for these types of sludges. There have also been indications that analyses for ⁹⁹Tc are higher than predicted by modeling at both SRL and Hanford. Waste characterization is ongoing with future emphasis on privatization and waste disposal.

New TPA (Tri-Party Agreement) strategy has Hanford tanks being sequenced for retrieval based on environmental risk. For tank S-112, ⁹⁹Tc is the main driver for risk. Assumptions for Tc⁹⁹ solubility significantly impact the risk results for allowable leak loss during retrieval, as well as allowable residuals after retrieval. Methods for evaluating and verifying the solubility and mobility of contaminates of concern, such as Tc⁹⁹, during retrieval and post retrieval operations is critical for developing risk based Leak detection, monitoring and mitigation strategies for SST retrieval. Methods must provide a high level of confidence to resolve risk uncertainties associated with tank farm retrieval performance evaluations.

Presently ⁹⁹Tc can be determined by radiochemical and ICP/MS techniques. When both techniques provide equivalent results they can be confidently reported. Presently, the amount of these comparison data is limited and occasional discrepancies are being seen. If the ⁹⁹Tc results are near decision limits for a project, higher confidence will be needed for the procedure. In this case, the use of inter-laboratory comparisons can be used to support the results. A ⁹⁹Tc workshop was held in September 1998 with the users of these data and the need for better ⁹⁹Tc data and methods of analyses was supported.

This study applies primarily to the DOE complex but could also be of value to privatization contractors doing work for DOE.

- ** | Schedule Requirements: Support M-45 Series Milestones for Tank Waste Closure Plans
- Definition of Solution:
- 15 * Targeted Focus Area: Tanks Focus Area (TFA) and Subsurface Contaminants Focus Area (SCFA)
- 16 **Potential Benefits:**
- 17 * | Potential Cost Savings: \$15,000,000 to \$20,000,000
- Potential Cost Savings Narrative: Potential cost savings are represented by a measurement method that assures the vendor and DOE that a true concentration of the ⁹⁹Tc has been measured, manifests of the waste and site are accurate, and the vendor or regulator should not have concern about the DOE-supplied concentration data. Current assumptions are that all technetium in tank waste is in the +7 valance state and is very mobile. This has an impact on long-term health risks and implications on retrieval system designs and leak mitigation requirements. An understanding of not only ⁹⁹Tc content, but distribution of it various valence states and their mobility and chemical stability can greatly influence risk assessment data. Better understanding of the actual form of technetium in tank wastes could result in more flexibility in using fluid-based retrieval system designs and leak mitigation provisions.
 - ** **Technical Basis:** Private vendors will receive LLW after it is characterized and concentrations of analytes documented. If sensitive analyte concentrations such as ⁹⁹Tc are inaccurately represented, the DOE will be responsible for the environmental and process rework caused. Without this interlaboratory testing and acceptance, the liability is likely to remain unresolved.

There has been an increased interest in defining the inventory and distribution of ⁹⁹Tc in the tanks. This interest also includes a better understanding of the speciation of technetium in the waste. Reliable ⁹⁹Tc methods will be required to provide the data to understand technetium behavior in Hanford Site tanks.

- 19 *Cultural/Stakeholder Basis:* Measurement data will have better credibility with the oversight panels when the measurement methodology has been peer-reviewed and accepted. Issues concerning emissions from the pretreatment and vitrification processes should be answerable with documented data.
- Environment, Safety, and Health Basis: Pertechnetates can be volatilized during processing of waste for vitrification. High concentrations not removed during pretreatment may be disbursed through the gaseous emissions during the vitrification process. Feed to the private vitrification vendor must be properly classified and manifested. Leakage during storage or retrieval operations may deposit waste containing ⁹⁹Tc into the soils surrounding the tanks. The mobility and long half-life of the isotope makes the concentration value significant for environmental consequences.

| 21 | Regulatory Drivers: The ⁹⁹ Tc concentration in feed streams classified as LLW are critical since the resulting vitrified product may contain inventory beyond the permitted quantities for onsite disposal. |
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| 22 * | Milestones: T04-01-W21, M-45-55-T01, M-45-55-T02 |
| 23 * | Material Streams: Sludge, Saltcake, Liquid (RL-HLW-20) |
| 24 | TSD System: N/A |
| 25 | <i>Major Contaminants:</i> Soluble, mobile +7 valence state of Technetium as well as insoluble +3 and +4 valence states; including impacts of complexants on increasing Technetium mobility. |
| 26 | Contaminated Media: Tank waste consisting of high molarity sodium hydroxide/sodium nitrate solution containing saturated saltcake and/or sludge. |
| 27 | <i>Volume/Size of Contaminated Media:</i> The single shell tanks are generally 75 ft. in diameter, and up to 40 feet deep with their tops buried about 10 feet below the ground surface. |
| 28 * | Earliest Date Required: 9/30/01 |
| 29 * | Latest Date Required: 2010 (Finalized Tank Waste Closure Plan) |
| Baseline Technology Information | |
| 30 | Baseline Technology/Process: The current baseline technology is radiochemical measurement of ⁹⁹ Tc. The alternative technology is ICP/MS. ICP/MS offers significant advantages in time required for analysis and reduced waste generation in the laboratory. However, the radiochemical technology could still be valuable for speciation studies. |
| | Technology Insertion Point(s): N/A |
| 31 | Life-Cycle Cost Using Baseline: |
| 32 | Uncertainty on Baseline Life-Cycle Cost: |
| 33 | Completion Date Using Baseline: |
| Points of Contact (POC) | |
| 34 | Contractor End User POCs: D.W. (Dennis) Crass, NHC, 509-372-2034, F/509-373-4311, Dennis W Crass@rl.gov |
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| 36 ** | Other Contacts: B.E. (Brian) Brendel, CE&ES, 509-373-1442, F/509-373-6101, Brian_E_Brendel@rl.gov J.W. (Jerry) Cammann, CHG, 509-372-2757, F/509-373-6101, Jerry W Cammann@rl.gov K.A. (Ken) Gasper, CHG, 509-373-1948, F/509-376-1788, Kenneth_A_Ken_Gasper@rl.gov |

^{*}Element of a Site Need Statement appearing in IPABS-IS
**Element of a Site Need Statement required by CHG